Writing good answers to AP Periodicity problems

November 15, 2012 by Adrian

In my experience, the majority of kids understand most of the chemistry behind the periodic trends typically asked in AP, free response questions, but way too often they cannot express that knowledge in succinct, meaningful English that allows (and encourages) the graders to award credit. As a result, students tend to score poorly on a topic that really ought to be an area that yields more points.

Below I have attempted to summarize some of the problems of expression (***not necessarily issues with understanding the chemistry***) to hopefully help to improve those answers and scores.

1. There is something that sits very poorly with me about the following sentence (and others like it).
"Sodium and magnesium are in the same shell'.
Sodium and magnesium are in the same *period*, and their *outer electrons* are in the same quantum level (shell) – there is a subtle, but important difference! I suggest applying 'quantum level' *only* to electrons, and 'period' to elements.

2. The use of term 'shielding' to describe the relative numbers of filled quantum levels between the outer electrons and the nucleus is absolutely fine, but I much prefer 'shielding' to be used *exclusively*in the context of describing ionization energy trends, and NOT when describing size trends.
When describing size trends, IMO it is better to refer to the number of 'occupied quantum levels' causing differences in size. Of course, 'occupied quantum levels' are directly related to shielding, but nevertheless.

3. A classic mistake is to re-state the question, and this can apply to many topic areas other than just periodicity, but it seems to be particularly popular, here.
If the question *states* that a particular trend is in play, e.g., 'The first ionization energy of neon is greater than that of lithium', then I have no interest in answers that start with sentences like, 'As you go across a period the first ionization energy increases'. We already KNOW that, the question told us! That habit inevitably leads us to a classic error in periodicity answers, i.e.,….

…..4. Never state the 'trend' as the *reason*. For example, it is **not** acceptable to state that the *reason*that neon has a higher first ionization than lithium, is that neon is further to the right in the period, and that ionization energy increase left to right on the table; (even though the second statement here, *is*true).

5. Answers that suggest it is harder to remove electrons from full, 'stable' shells, are not my favorite thing, either. For example, the reason Ca's 3rd ionization energy is so much higher than its first and second, is ***not***that Ca^{2+} is 'stable' and has a 'noble gas configuration'. Rather it is because the third electron is being removed from 3p sub-level (as opposed to 4s sub-level), which is closer to the nucleus and the shielding is less making the attraction stronger.

6. I am a huge fan of writing the electronic configurations of any species involved in ionization energy difference questions. This very often partially answers the question anyway, but in any case it can make it much easier for the student to 'see' the answer.
For example, if we actually *write* the electronic configurations for Ne and Na as part of the answer when explaining the differences in their first ionization energy (Ne: $1s^2\ 2s^2\ 2p^6$ and Na: $1s^2\ 2s^2\ 2p^6 3s^1$), then there is immediately an obvious difference in the quantum shell where that first electron resides. The written electronic configurations act like 'diagrams', in as much as they help to explain and 'illustrate' what many, garbled words may fail to do. For that reason, I say write electronic configurations when comparing ionization energies.
Oh, and one more thing. Make sure you are looking at the Periodic Table that comes with the examwhen you are answering these questions!

Writing good answers to AP Bonding problems

January 1, 2013 by Adrian

Updated 11/16/13

Again, here I am not really trying to address the chemistry per se, rather I'm trying to address the *way*kids write their answers. The language, phraseology, the common misconceptions & pitfalls, and how they generally screw-up when trying to transfer what is in their head on to the paper in front of them.

1. The word *molecule* should never be used when discussing ionic compounds. Molecules are small groups of covalently bonded atoms, and do not exist in ionic substances.

2. Ionic compounds don't contain atoms, and covalent molecules don't contain ions. While we're at it, there no such thing as a 'water atom', either!

3. A hydrogen bond is an intermolecular force (IMF), NOT an intra, covalent bond between a hydrogen atom and another atom. A particular pet peeve of mine is the use (by students) of the phrase, 'Water is a hydrogen bond'. PLEASE get into the habit of re-phrasing to say, 'The IMF's between water molecules are hydrogen bonds'.

4. London Dispersion Forces exist as IMF's between ALL molecules, but they may not be the correct answer when considering what I call, 'the spirit of the question'. For example, it would be an extremely unusual question, that when asking about the IMF's between molecules of say, HCl, expected an answer that talked *exclusively* about LDF's and not dipole-dipole attractions.

5. London dispersion forces DO increase with size, but you had better be REALLY careful saying such. In recent years, the AP readers have been very keen to make sure that YOU know that 'size' does not mean 'mass'.
LDF's are not gravitational forces between two very large masses like planets, rather they are electrostatic forces that depend on the number of electrons present and the surface area of the atoms/molecules. Of course, it is true that with more electrons and larger atoms that mass does increase as well, but make it clear that you know that the LDF is not dependent upon mass per se.

6. In relation to #5, AP readers have recently been very keen for you to use the words, '*increased polarizability*' to help make the distinction when explaining the increases in intermolecular attractions that come with larger molecules and atoms.

7. Don't apply the concept of IMF's (of any kind) to ionic compounds. Ionic compounds are held together with ionic bonds and contain no molecules so also contain no inter-molecular forces.

8. When comparing the boiling points of a couple of substances where the IMF's are different, do two things. Firstly talk about **both** substances in terms of identifying the IMF's present (a common complaint from readers is the students only talk about one of the substances), and secondly, state clearly which force is the stronger of the two.
Declaring for example, that 'hydrogen bonding is present between molecules of X', without mentioning the other substance, OR that hydrogen bonding is a relatively strong IMF, is unlikely to cut it.

9. Avoid the phrase, *'sodium chloride is polar'* (insert any ionic compound you choose). Although it could be argued that ionic compounds are the *ultimate* in polarity (completely separated charges with a MEGA-dipoles), don't! The word 'polar' is much better off being exclusively used in relation to covalently bonded molecules.

10. Most AP questions that ask about shape are likely to be asking about the geometry of the *atoms*, not the geometry of the electron domains (that include lone pairs), but either way, be sure to state what you are referring to, clearly.

11. There's little or no point in ever attempting to compare the strength of an ionic and covalent bond. You will never be comparing like-with-like, so I don't think comparisons are really all that helpful. For example, you can never compare the ionic and covalent bond strengths between Na and Cl, since no covalent bond exists between the two. Likewise, it is not ever going to be possible to compare the 'ionic bond' between two chlorine atoms to the covalent bond that *does* exist between them.

12. You certainly *can* draw Lewis diagrams for individual, simple, monatomic ions, since in their purest form we are only talking about representing outer shell electrons, but to be honest, in virtually all cases, Lewis diagrams are better used only for covalent compounds and for showing the covalent bonds *within*, polyatomic ions.

13. Atoms, not molecules, have differences in electronegativity.

14. Take great care to distinguish between the polarity of a bond, and the polarity of the overall molecule – they are different things.

Writing good answers to AP Kinetics problems

February 17, 2014 by Adrian

Here's the latest in the 'writing good answers' series, *Writing good answers to AP Kinetics problems*.
Most of these tips are based upon free response questions from the old curriculum, simply because as yet we having nothing else to go on, but having said that, all of these ideas are likely to still remain relevant going forward. Here we go in no particular order.

1. When deriving a rate law from initial rate data in a FRQ, in nearly all cases it will be necessary to justify your answer by showing some kind of work. Essentially there are three ways to do this;
Firstly one could write a paragraph of prose, outlining which experiments are being compared, which reactant concentrations change and which are are kept constant, followed by an explanation of how that affects the rate, and therefore derive the order with respect to the reactant that changed. That can get VERY messy, very quickly, especially when a set of data has one of those annoying combinations that fail to give you a pair of experiments that keep one of the reactants constant while changing another. As a result I generally don't advise the 'prose method'.
Secondly, one can set up what I call a 'table of comparisons'. For example, from the initial rate data shown below;

Expt.	**[A]**	**[B]**	**Relative Rate**
1	1.0	1.0	1
2	1.0	2.0	2
3	2.0	1.0	4

I would construct this 'table of comparisons';

Compare Expt.'s	**[A]**	**[B]**	**Relative Rates**	**Orders**
1 and 2	x1	x2	x2	1st order wrt [B]
1 and 3	x2	x1	x4	2nd order wrt [A]

Thirdly, use the 'math method'. The math method is preferred by me when there is unhelpful data (as described above) that fails to keep a particular reactant constant while investigating another. Take for example, the data table of initial rates that appears in FRQ 1997, 4, where an investigation of the [B] on the rate is always clouded by the simultaneous change of [A].

Experiment	**Initial [A]**	**Initial [B]**	**Initial Rate of Formation of C (mol L^{-1} min^{-1})**
1	0.25	0.75	4.3×10^{-4}
2	0.75	0.75	1.3×10^{-3}
3	1.50	1.50	5.3×10^{-3}
4	1.75	??	8.0×10^{-3}

Here, the order with respect to [A] is established easily (and the 'math method' is not really necessary), but carrying the order with respect to [A] forward to the second 'math method', makes finding the order with respect to [B] relatively easy (which would not be the case without the use of the 'math method').

$$\frac{\text{Rate}_1 = 4.3 \times 10^{-4} = \cancel{k}\,[0.25]^a\;\cancel{[0.75]^b}}{\text{Rate}_2 = 1.3 \times 10^{-3} = \cancel{k}\,[0.75]^a\;\cancel{[0.75]^b}} = \frac{1}{3} = \left(\frac{1}{3}\right)^a \text{, so a = 1}$$

and the order wrt [A] is first

Having established a = 1, use it in the expression below;

$$\frac{\text{Rate}_2 = 1.3 \times 10^{-3} = \cancel{k}\,[0.75]^1\,[0.75]^b}{\text{Rate}_3 = 5.3 \times 10^{-3} = \cancel{k}\,[1.50]^1\,[1.50]^b} = \frac{1}{4} = \frac{1}{2}\left(\frac{1}{2}\right)^b \text{, so b = 1}$$

and the order wrt [B] is first

2. The units for rate constants are almost always subject to a scoring point so ensure that you understand how to get this right!

3. In most cases on the AP exam in the past, if an intermediate appears in the slow step of the reaction, it is replaced by the reactant that it depends upon in a fast equilibrium step. Look out for intermediates that lead to fractional rates as in 2009.

4. The (full) justification of a mechanism usually requires three, separate considerations;
i. Do the reactants of the slow step match the species that are in the rate law?
ii. Does the stoichiometry of the slow step match the orders in the rate law?
iii. Do the individual steps of the mechanism add up to the overall stoichiometry of the equation?
Not all questions necessarily require all of these, but you had better be prepared to give each one in various situations.

5. Be aware that 'rates' are sometimes expressed as shown below. It's nothing new, but don't let either the signs, or the use of Delta confuse you. Generally it has *not* been necessary to to use negative signs to show a reactant concentration declining, but just be aware of the simple relationship between signs and concentrations either increasing or decreasing.

$$Rate = -\frac{\Delta[Reactant]}{\Delta time} \qquad \textbf{OR} \qquad Rate = \frac{\Delta[Product]}{\Delta time}$$

6. Another thing to be aware of is the idea that rate constants can be expressed in more than one way. Consider this reaction and data from 2008, 3.

$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$

Experiment	Initial Concentration of NO (mol L^{-1})	Initial Concentration of O_2 (mol L^{-1})	Initial Rate of Formation of NO_2 (mol L^{-1} s^{-1})
1	0.0200	0.0300	8.52×10^{-2}
2	0.0200	0.0900	2.56×10^{-1}
3	0.0600	0.0300	7.67×10^{-1}

Leading to this rate law:

$$\text{rate} = k[NO]^2[O_2]$$

And in turn to this expression for k:

$$k = \frac{\text{reaction rate}}{[NO]^2[O_2]}$$

OK, so far so good, here's where one of two things can occur.
a. If we assume the rate of the reaction *is the same* as the rate of formation of NO_2, then simply substitute in values from experiment #1, according to;

$$k = \frac{8.52 \text{ x } 10^{-2} molL^{-1}s^{-1}}{(0.0200\ molL^{-1})^2(0.0300\ molL^{-1})} = 7.10 \text{ x } 10^3\ L^2\ mol^{-2}\ s^{-1}$$

This is what I usually do, never bothering with b. below.
b. There is another situation that requires that the rate constant, k, be different to a reflect a coefficient of 1. In this case, because the stoichiometric number for the compound that is used to monitor the rate (NO_2) is 2, then we must half the rate, to reduce the coefficient to 1, and hence get a value of 3.55 x 10^3 L^2 mol^{-2} s^{-1} according to the calculation below.

$$k = \frac{\left(\frac{1}{2}\right)(8.52 \times 10^{-2}\ \text{mol L}^{-1}\text{s}^{-1})}{(0.0200\ \text{mol L}^{-1})^2(0.0300\ \text{mol L}^{-1})}$$

$$= 3.55 \times 10^3\ \text{L}^2\ \text{mol}^{-2}\text{s}^{-1}$$

To my knowledge this has only ever come up once, in this particular free-response question from 2008, and even then, either answer for k was accepted. If one method over the other was required, I would imagine that the question would need to be more/very specific.

7. When justifying an order when 'straight line' graphical data is presented, there is some *potentially*conflicting information presented in the scoring standards by the College Board. For example, when comparing the official answers for 2005B, 3 and 2011, 6, in one case in was apparently OK to simply say, 'It is '0/1/2' order because the graph of '[X] / ln[X] / $[X]^{-1}$ versus time is a straight line', and in the other case it appears that more was expected, i.e., that the answer required a more than just a reference to the fact a straight line was produced.
This is easy to do if the order in question is zero, since one can say that the changing concentration of X leads to no change in the slope of the graph, i.e., no change of rate so it must be zero order, but to justify it for first or second order plots, where ln[X] and $[X]^{-1}$ lead to straight lines, seems to me to require more math than is reasonable *in the context of an AP chemistry exam*.

In short, for zero order justifications in straight line graph situations, I would be inclined to always add a few words of explanation (as above), but for first and second order straight line graph situations, I would be inclined to simply limit my justification to saying that, '*the plot of ln[X] or [X]$^{-1}$ yields a straight line*'. This may explain the differences in the two, College Board scoring standards.

EDIT 04/29/15.
A note on questions that ask about collision orientation. I have now seen this on multiple occasions in a manner I have not seen (or at least noticed) in the past.
When talking about a reaction needing the correct orientation as one of the criteria for a successful collision, it seems as though answers are now going beyond simply saying 'a specific, correct orientation is required', and they appear to be wanting some mention of the bonds that are broken and those that are made.
So, in this example, which is for this reaction, Cl + NOCl ==> Cl_2 + NO, it *may* be necessary to say that the Cl must collide with the Cl in NOCl, in order to make a bond between the two chlorine atoms, and if that does not happen, no reaction occurs. We all knew this anyway, but I have seen more than one example where specific atoms (apparently) needed to be referenced.

Writing good answers to AP Equilibrium problems

February 24, 2016 by Adrian

Here's the latest in the 'writing good answers' series, *Writing good answers to AP Equilibrium problems*.
This post only deals with aspects of equilibria such as Kc, Kp, Ksp and Le Châtelier's Principle .So, here's a list of some pointers to make your AP equilibrium answers a little better.

1. When writing a Kp expression, refrain from using square brackets. For example, it would be incorrect to write, Kp = [pp CO_2], for the equilibrium system $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$. Why? Well square brackets actually have a meaning, i.e, concentration, and a Kp expression is one where partial pressures are being used.

2. Remember what K actually means! K expressions are ratios of various aspects of products and reactants *at the equilibrium position*, meaning that ***initial*** concentrations/partial pressures do NOT go into them. Of course, this means dealing with ICE tables, but it also means ***that sometimes we don't need to deal with ICE tables IF we are given the equilibrium concentrations***.

3. Since $\Delta G° = – RT \ln K$, then ΔG° is associated with equilibrium. This means that equilibrium must be established before the calculation of ΔG°, and that ΔG° is actually a measure of the ratio of reactants to products *once equilibrium has been established*.

4. When performing a calculation to predict if a precipitate is formed using the reaction quotient Q, (e.g., when considering the generic reaction $MX_{(s)} \rightleftharpoons M^{2+}_{(aq)} + X^{2-}_{(aq)}$ and determining if a precipitate forms), when one finds that Q is too small (and therefore no precipitate is formed), it's not a good idea to say, "The equilibrium continues to shift forward to make Q bigger in order for it to equal K so no ppt. forms". This isn't the case, since the equilibrium *has not even been established at this point* so it can't 'move forward' per se. It would be better to say that Q is not currently sufficiently large enough to create the ppt. This is the same as saying that Q is not yet large enough to create the backward reaction, so the equilibrium has not been established.

5. Can one use a simple, 'reduce the stress' (Le Châtelier) argument when dealing with an explanation of shifting equilibria, or does one need to invoke a 'Q versus K' argument? **This is a GREAT question and honestly one that remains unresolved unless the question *specifically*asks you to discuss Q and K**. I wrote an entirely separate blog post about this, and it is my belief that the 'Q versus K' argument is going to be anticipated/expected/required more and more on the new exam.
This brings up another prickly question, about how deep a student is supposed to understand WHY an equilibrium system shifts in the endothermic direction when heated. I've dealt with that here, but with *quantitative* Arrhenius off the table in the new exam, I suspect this is simply not required. As such, it seems OK (for now) to treat 'heat' as either a product (exothermic) or a reactant (endothermic), and reason via Le Châtelier. If one *insisted* on using a 'Q versus K' argument, one ought to be able to get away with commenting on the fact that for an exothermic reaction K is smaller at higher temperatures (without further explanation), and that a reaction will shift to make Q equal to K (and vice-versa).

6. Question 1(g) from 2004 has created some issues for students or more precisely, it's the published answer that causes issues. Kids Google the answer, really don't understand it at all, and end up simply quoting "*the concentration is independent of the volume*" without a clue what that statement actually means. I think it better to say that on the removal of water, the concentrations of the ions instantaneously increase, making Q (temporarily) bigger, causing a shift backwards to make Q smaller (and to make more solid), and thus return Q to the K value. In turn, this restores the original concentrations. Vice-versa for the addition of water to such a system.

7. Whenever you decide to neglect 'x' in a Ksp/common ion problem because it is so small, say so! What I mean by that is make it clear why you have decided that 'x' is negligible. Of course, this applies to weak acids and bases too. By stating the fact that you know what you are doing, you are removing any ambiguity that you may just have forgotten about it!

8. Be very careful when using Ksp values to compare solubilities. 'Solubility' refers to the 's' or 'x' value (in units of g or mol per unit volume) from the ICE table, and Ksp is by definition, the 'product' of such (mol/L) values raised to appropriate powers.

Each salt has its own molar solubility (again, the 's' or the 'x' value in the ICE table), that will then manifest itself differently depending on the exact nature of the Ksp expression. As such, you should be comparing the 's' (or 'x') values rather than the Ksp's when comparing solubilities. This means that rather than simply saying, "Oh, *this* Ksp is smaller than *that* Ksp so the first salt is less soluble", one actually has to undo the Ksp expression and calculate a value for 's' (or 'x') before making the comparison.

Writing good answers to AP Acid-Base problems

March 11, 2016 by Adrian

Here's the latest in the 'writing good answers' series, *Writing good answers to AP Acid-Base problems*.
It's probably the toughest topic on the exam for students, or at least it seems to be, so here are a few pointers that might help when answering questions on acid and bases on the AP chemistry exam.

1. You may treat the addition of the salt of a weak acid (the conjugate base) to a solution of the same weak acid as either a buffer problem, or as a common ion problem (and the same is true of the addition of the salt of a weak base (the conjugate acid) being added to a solution of the same weak base). I prefer to treat it as a buffer, and pick up the Henderson-Hasselbalch equation immediately, but you may prefer a common ion approach. Either works.

2. Significant figures on pH problems may not ever be an issue (mainly because the College Board is in a complete mess when it comes to significant figures with no official word on how they will be treated – see this and this), BUT if you want to get sig figs in pH calculations correct, see this.

3. When asked to write a Ka (or Kb) expression, don't jump directly to the $[H_3O^+]$ or $[OH^-]$ squared numerator. They don't like that. e.g., for the reaction
$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$
Write Ka as

$$\frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

and not as

$$\frac{[H_3O^+]^2}{[CH_3COOH]}$$

Even though they are numerically the same thing, and the second one will be the one that you effectively use when doing any kind of calculation on the weak acid, always write the top one first.

4. If you decide to neglect the degree to which a weak aid or base ionizes, i.e., you treat the 'x' decrease of the moles of the weak acid or base as negligible in order to avoid a quadratic, then SAY so! Tell the examiner you have left it out on purpose. (As an aside, occasionally you'll come across a problem where you may be given the 'x' value and in that case I would tend to include it in the calculation of the equilibrium moles of the weak acid or base).

5. Increasingly (perhaps even always), it's not going to be sufficient to justify/explain why when a weak acid or weak base is involved in a titration, that the pH at the equivalence point is not 7 by simply saying "the strong acid (or base) 'wins'". Obviously this was never really an explanation anyway. You should always reference the relevant hydrolysis reaction and increasingly likely IMO, you may *have* to write said reaction.
For example, when ethanoic acid has been completely neutralized by a strong base, the resulting salt (the ethanoate) will hydrolyze at the equivalence point according to the equation below, thus making the solution basic at this point.
$CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$

6. There is a new emphasis on the exam for you to be able to qualitatively see that the further the pH of a buffer is from its pKa, then the further the log of the ratio of [salt]/[acid] is from zero, i.e., the further the ratio is from 1:1. Ratio's that favor the salt (i.e., those greater than 1) cause the pH > pKa, and those that favor the acid (i.e., those less than 1) cause pH < pKa.

7. Another emphasis (that is essentially the SAME as #6 above) seems to be that there should be a qualitative understanding (rather than actually plotting a bunch of pH values on a pH curve), that the pH during the titration of a weak acid or weak base with a strong base or strong acid, varies only by about 1 unit for about 80% of the buffer region, with larger changes at the beginning and end of that region where ratios of salt:acid are relatively far from 1, and close to horizontal near the middle of the region where the ratio of salt to acid is close to 1.

8. Don't make the mistake of thinking that Kw = (Ka)(Kb) for *any,* random weak acid and weak base – they have to be a conjugate pair! I've seen it, trust me!

9. Another new emphasis is the idea that neutrality is based upon the relative concentrations of hydroxide and hydronium ions, and NOT the pH. Only at 298 K (when $K_w = 1 \times 10^{-14}$) is a pH of 7 considered neutral, and in all situations you should be comparing $[OH^-]$ with $[H_3O^+]$ to determine the acidity, basicity or neutrality of the solution.